February 1999

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Langmuir monolayers as disordered solids: Strain-tilt-backbone coupling and natural order parameters for the swiveling transitions

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(Received 31 August 1998; accepted 29 October 1998)

Multistability of Langmuir monolayers, in particular those composed of fatty acids, is reflected by a very rich and complicated phase diagram. We argue that strain-tilt-backbone coupling determines the behavior described by that diagram. Following the solid state approach, we show that a natural order parameter set is defined by thermal averages of spherical harmonics and strain tensor components. In addition, we show that the backbone order parameter can be conveniently represented by an elastic dipole tensor. Treating Langmuir monolayers as disordered solids, we have derived an orientational entropy contribution to the free energy. The swiveling transition between $L_2(L_{2h})$ and $L_2'(L_2^*)$ phases is discussed in detail and is conveniently described in terms of the proposed order parameters. We discuss why the change in the distortion direction of the 2D unit cell tracks the change in tilt direction of the molecules, and also why the cell dimensions involved in the swiveling transition are the same in both phases. © *1999 American Institute of Physics.* [S0021-9606(99)71305-X]

I. INTRODUCTION

Molecular monolayers at the air-water interface exhibit very rich thermodynamical behavior. They form a variety of phases with different degrees of translational and orientational disorder from gas-like to solid-like phases.[1] The surface pressure-temperature (π-T) diagrams of saturated fatty acids, especially in the region of condensed phases with all their complications and similarities, allow the establishment of a generic phase diagram.[2,3] This diagram is presently used as the foundation to discuss the phase behavior of Langmuir monolayers (Fig. 1).

There are ongoing experimental, theoretical, and numerical attempts to gain more knowledge about the molecular nature of the different phases and the transitions between them. Is it the conformation of the individual alkane chains or their interaction and dynamics (or both) which govern the structures of the different phases of the molecular monolayers? In recent years there has been impressive progress in experimental structural determinations,[4] although there is still unresolved ambiguity in the assignment of phases as crystalline or mesophase.[5] The phases are distinguished by widths of diffraction peaks, but the interpretation of the broad peaks in some phases as hexatic (mesophase) is questioned based on finite resolution. Apart from the fact that the hexatic phase has been proposed for purely 2D systems and Langmuir monolayers are only quasi-two-dimensional, the diffraction patterns of mesophases can be understood with the ideas of positional and orientational disorder. We shall, following our previous suggestions[3] and other work, advocate the concept of Langmuir monolayers as disordered solids.[6]

Theoretical attempts to describe the symmetries of the phases in the generic (π-T) phase diagram attack the problem from two opposite viewpoints: liquid-crystalline or solid state. But it is always the hexagonal, high-pressure (LS) phase which serves as the highest symmetry, parent phase. Selinger and Nelson[7,8] developed a Landau theory for the hexagonal lattices using an azimuthal angle, ϕ, as the only order parameter. Kaganer and Loginov[9,10] have worked out a phenomenological Landau-type theory which describes orientational order via the order parameter, $\eta = \sin\theta$, where θ is the molecular tilt angle, and the azimuthal angle ϕ which describes the tilt direction. Additionally, a symmetric 2D traceless tensor, $Q_{ij} = N_i N_j - 1/2\delta_{ij}$, analogous to the nematic order parameter for liquid crystals, has been used to characterize the orientation of the backbone planes of the molecules. The positional or translational order was also characterized by so-called weak crystallization order parameters, which describe herringbone order as well. However, an important structural aspect, the distortion of the hexagonal lattice, was not uniquely defined nor considered. Advocating the liquid-crystalline approach, Kaganer *et al.*[4] have recently characterized the distortions with respect to a hexagonal lattice using two concepts: the so-called distortion ellipse[11] and the ''projected unit cell.'' [12] With so many parameters, the theory not only became less transparent but also did not help us to understand and to describe phases observed in the generic phase diagram. In particular, the swiveling transition, recently studied in detail,[12,13] provides an example which can critically test current theoretical descriptions of Langmuir monolayers.

The solid state approach that we advocate[3,6,14] has all the advantages of the phenomenological Landau theory and additionally allows for a more clear characterization of the ori-

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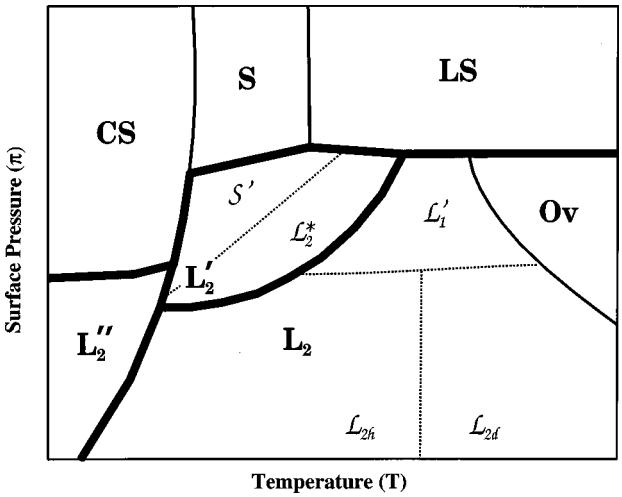

FIG. 1. Composite π-T phase diagram for Langmuir monolayers (see Ref. 3).

entational ordering (via spherical harmonics) and structural distortions from the hexagonal phase (via external strain tensor components). In particular, it is better suited to deal with the problem of tilt-strain coupling responsible for transitions like the swiveling one. The aim of this article is to expand our previous theory,[3] include the backbone order parameter, show how the molecular cross section can be represented by an internal strain, and then apply the theory to the swiveling transitions. We shall illustrate the tilt-strain coupling by numerical calculations.[6]

II. THE MODEL

In our approach,[3,14] a monolayer system is modeled as orientationally free tails grafted to a 2D net formed by the head groups of the amphiphilic molecules. Following the microscopic derivation,[3] the system energy can be described as

$$V(\{\epsilon\},\{\Omega\}) = V^R(\{\Omega\}) + V^{TR}(\{\epsilon\},\{\Omega\}) + V^T(\{\epsilon\}). \quad (1)$$

The orientational part of the potential can be expressed in terms of rotational matrices $D(\Omega)$. The angular variables which form the set $\{\Omega\}$ are the Eulerian angles representing molecular orientations. The translational part of the system energy is conveniently expressed in terms of external strain tensor components, $\{\epsilon_{ij}\}$. The second term in the total energy represents the coupling between these two types of variables. As has been discussed,[3,6] the translational contributions to the energy may be viewed as coming from both the head groups and molecular tails.

The orientational potential for a system with large expected orientational fluctuations has to be expressed in terms of symmetry adapted rotation functions, the Wigner functions. For a Langmuir monolayer for which we have chosen the hexagonal, untilted phase (LS) as a parent phase, this means a set of surface harmonics (composed of spherical harmonics) adapted for C_{6v} symmetry,[3]

$Y_1 \approx \eta \cos\phi$ and $Y_2 \approx \eta \sin\phi$, belong to the doubly degenerate E_1 representation,

$Y_3 \approx (3\cos^2\phi - 1)$, belongs to the totally symmetric A_1 representation, and

$Y_4 \approx \eta^2 \cos 2\phi$ and $Y_5 \approx \eta^2 \sin 2\phi$, transform as components of the doubly degenerate E_2 representation.

This set of spherical harmonics describes orientational fluctuations of molecular tails in terms of tilt (θ) and azimuthal (ϕ) angles and allows for the simplest description of the rotational potential. The description is exact when the molecules are treated as rigid rods, e.g., when their effective cross section is well approximated by a circle. This is true for the rotational phases, of which the parent hexagonal LS phase is one. We have used such a set in our theory where the molecular tails have been averaged to cylindrical shape. Strictly speaking, the functions describe orientational fluctuations of the tails assuming (almost) free rotation about the long axis. The functions Y_1 and Y_2 transform as x and y components of a vector, while Y_3, Y_4, and Y_5 transform as components of a second rank tensor. The symmetry properties of the harmonics are very important because they allow relation of every observable property, vectorial and/or tensorial, to statistical averages of the corresponding surface harmonics.

The translational part of the energy is conveniently described in terms of the strain tensor for the 2D net. The variables $e_{xx} - e_{yy} = \epsilon_2$ and $e_{xy} = \epsilon_6$ transform as components of the E_2 representation, while $e_{xx} + e_{yy} = \epsilon_1$ transforms as the totally symmetric A_1 representation. The non-symmetric strain variables take the following form for the hexagonal C_{6v} reference cell,[6]

$$\epsilon_2 = 1/a_0[(2/\sqrt{3})a_1 \sin\gamma_1 - b_1]$$

and

$$\epsilon_6 = 1/(2\sqrt{3}a_0)[b_1 - 2a_1\cos\gamma_1], \quad (2)$$

where a and b are the lengths of the 2D lattice vectors and γ is the angle between the vectors in reciprocal space. Since the strains ϵ_2 and ϵ_6 transform as components of the doubly degenerate E_2 representation, they can be written in analogy to surface harmonics Y_4 and Y_5, as $\epsilon_2 = \xi\cos 2\beta$ and $\epsilon_6 = \xi \sin 2\beta$. The distortion amplitude may then be identified as $\xi = 2a_1/\sqrt{3}a_0[\sin\gamma_1 - \sqrt{3}\cos\gamma_1]$, where a_0 is the lattice period before deformation. The angle β defines the direction of the lattice deformation, and for $\beta = 0, \pi, \ldots$, it is along the nearest-neighbor (NN) direction, contracting for $\xi < 0$ and stretching for $\xi > 0$. The strain $\epsilon_2 \neq 0$ describes a deformation of the lattice from hexagonal to rectangular symmetry, while $\epsilon_6 \neq 0$ defines distortion to an oblique lattice. It is important to realize that the strain parameters appear very naturally from the symmetry analysis and the identification as above has an advantage over the description recently proposed,[4] where the suggested formula for the distortion order parameter is: $(a^2 - b^2)/(a^2 + b^2)$, where a and b are the major and minor axes of an ellipse drawn through the six nearest neighbors of a hexagonal net. This choice of deformation parameter is less general, and additionally shows a complicated relation to two-dimensional crystallography.

Having identified the symmetry properties of the orientational and strain variables, we can write the contributions to the free energy as follows:

$$F^R = a(\langle Y_4\rangle^2 + \langle Y_5\rangle^2) + b(\langle Y_4\rangle^3 - 3\langle Y_4\rangle\langle Y_5\rangle^2) + c(\langle Y_4\rangle^2 + \langle Y_5\rangle^2)^2 + f(\langle Y_1\rangle, \langle Y_2\rangle), \quad (3)$$

$$F^T = 1/2C_{66}^0(\epsilon_2^2 + \epsilon_6^2) + A(\epsilon_2^3 - \epsilon_2\epsilon_6^2) + B(\epsilon_2^2 + \epsilon_6^2)^2, \quad (4)$$

$$F^{TR} = \alpha(\epsilon_2\langle Y_4\rangle + \epsilon_6\langle Y_5\rangle). \quad (5)$$

Thermal averages of the surface harmonics are taken with the total potential of the system given by Eq. (1). It is important to notice that this free energy function describes transitions from the LS, hexagonal parent phase to distorted and/or tilted phases without a translational symmetry change. As has been extensively discussed, transitions to herringbone architecture (and ordering) of the tilted molecules is conveniently described by the same orientational order parameters but including a wave-vector dependence.[3]

The most important feature of the free energy function is bilinear coupling between tensorial order parameters, orientational fluctuations, and strains. The fluctuations described by vectorial parameters $\langle Y_1\rangle$ and $\langle Y_2\rangle$ are responsible for transitions to tilted phases within hexagonal nets, and because they do not couple linearly with strains, we shall neglect their contribution. The bilinear coupling in the translational-rotational part of the free energy follows from the symmetry of the system and results in the relations, $\langle Y_4\rangle \propto \epsilon_2$ and $\langle Y_5\rangle \propto \epsilon_6$. The linear dependencies have been shown experimentally,[4] (described as $\xi \approx \eta^2$) which is a simple consequence of the symmetry considerations and the more general relation between natural order parameters. It is clear that the parameter sets $\{\langle Y_4\rangle, \langle Y_5\rangle\}$ and $\{\epsilon_2, \epsilon_6\}$ are equivalent, and it is a matter of taste which of them will be used to characterize phases and phase transitions. If one would like to stress the elastic aspects of a transition, as is the case for ferroelastic transitions in monolayers, the free energy functional will be expressed as a polynomial in terms of the strain order parameters.[14] However, for Langmuir monolayers, it is much more common to stress the orientational order of the molecules and thus we shall express the free energy in terms of the thermal averages of the surface harmonics. From a minimization of the total free energy with respect to strain components, the free energy function is

$$F = a'(T)[\langle Y_4\rangle^2 + \langle Y_5\rangle^2] + b'(T)[\langle Y_4\rangle^3 - 3\langle Y_4\rangle\langle Y_5\rangle^2] + c'(T)[\langle Y_4\rangle^2 + \langle Y_5\rangle^2]^2. \quad (6)$$

The coefficients are renormalized with respect to those in Eq. (3) and they are, in general, temperature dependent. For the quadratic term, the dependence can be justified in a simple approximation by calculating the rotational susceptibility, $\chi = (kT)^{-1}\langle Y^2\rangle$, as shown in the previous paper.[3] Here, we shall show how the temperature dependence can follow from the orientational entropy, assuming, therefore, a kind of orientational disorder within the monolayers. This seems quite reasonable for systems that we consider as disordered solids. The temperature dependencies of the parameters will determine the shape of the free energy function. We expect that for some temperature region the function represents a ''Mexican hat'' with three minima located away from the center point which represents the LS, hexagonal phase. The minima would then correspond to three domains of a tilted (and correspondingly deformed) ferroelastic phase. The swiveling transition would then be identified as a transition between two ferroelastic phases.

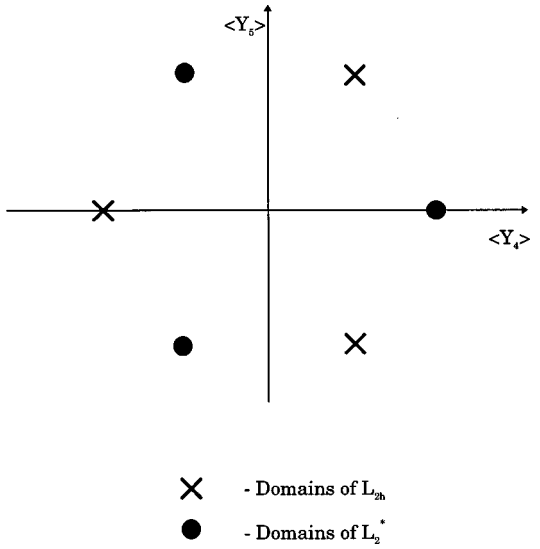

FIG. 2. Domains of the ferroelastic L_{2h} and L_2^* phases presented on the plane of the orientational order parameters $\langle Y_4\rangle, \langle Y_5\rangle$. The domains correspond to minima of the free energy function, Eq. (6).

III. THE ORIENTATIONAL ENTROPY

The orientational order of the molecules at a temperature T can be described by a single particle orientational distribution function, $P(\Omega)$. The probability that the molecule has its axis directed within the solid angle $d\Omega = \sin\theta d\theta d\phi$, about the direction $\Omega = (\theta, \phi)$ is given by $P(\Omega)d\Omega$. The orientational distribution function can be expressed in terms of the symmetry-adapted spherical harmonics and, for highly delocalized orientations, higher order harmonics are needed to describe the function. For a system with C_{6v} symmetry, we would expect six states ($\phi_i = i2\pi/6$, $i = 1,..6$) which reflect localization of the orientations of the molecules. However, as is evident from the above symmetry considerations, only three of them are strongly coupled with the strains. As has been shown in many experiments for Langmuir monolayers, the orientational fluctuations are strongly coupled with the strains and for this reason we may assume that there are three ''pocket states'' which contribute to the orientational distribution function for the strain-orientation coupled system. The states are defined as $\Omega_j = (\theta, \phi_j)$, $j = 1,2,3$ with $\phi_1 = 0$, $\phi_2 = 2\pi/3$ and $\phi_3 = 4\pi/3$ (Fig. 2). If the pocket states are approximated by delta functions, the averages of the surface harmonics are

$$\langle Y_4\rangle = \eta^2 \Sigma P_j \cos 2\phi_j, \quad \langle Y_5\rangle = \eta^2 \Sigma P_j \sin 2\phi_j, \quad (7)$$

where $\eta = \sin\theta$, as previously defined. From these equations, we have the following relations:

$$P_1 = 1/3 + 2/3\langle Y_4\rangle, \quad (8a)$$

$$P_2 = 1/3 - 1/3\langle Y_4\rangle + 1/\sqrt{3}\langle Y_5\rangle, \quad (8b)$$

$$P_3 = 1/3 - 1/3\langle Y_4\rangle - 1/\sqrt{3}\langle Y_5\rangle. \quad (8c)$$

The contribution to the orientational entropy is therefore approximated by

$$S \cong -NK\Sigma P_j \ln P_j, \tag{9}$$

where N is the number of molecules and k is Boltzmann's constant. Using the above relations for the orientational distribution and expanding for small values of the order parameters, the orientational entropy energy contribution per molecule is,

$$-(1/N)TS = -\text{const}\, T + kT(\langle Y_4\rangle^2 + \langle Y_5\rangle^2) - kT(\langle Y_4\rangle^3 - 3\langle Y_4\rangle\langle Y_5\rangle^2) + 3/2kT(\langle Y_4\rangle^2 + \langle Y_5\rangle^2)^2. \tag{10}$$

Within this approximation, which assumes a certain degree of disorder between three states in the hexagonal parent phase, the free energy is described by the function Eq. (6), with coefficients being linearly dependent on the temperature. For example, $a'(T) = a' + kT$, where $a' = a - \alpha^2/C_{66}^0$, but $b'(T) = b' - kT$ and the opposite effect of the temperature will decide the relative stability of different phases.

If one includes the surface pressure effect, the Gibbs free energy is written as

$$G(T, \pi) = F(T) + \pi\epsilon_1, \tag{11}$$

assuming that the 2D pressure is isotropic and couples with the totally symmetric strain $\epsilon_1 = (e_{xx} + e_{yy})$ only. This assumption might not be fulfilled by experimental conditions.

Now, the free energy of the system expressed in terms of the orientational order parameters determines three domains that are characterized by the molecular orientations

$$\langle Y_4\rangle; \quad -1/2\langle Y_4\rangle + \sqrt{3}/2\langle Y_5\rangle; \quad -1/2\langle Y_4\rangle - \sqrt{3}/2\langle Y_5\rangle, \tag{12}$$

and the corresponding strains

$$\epsilon_2; \quad -1/2\epsilon_2 + \sqrt{3}/2\epsilon_6; \quad -1/2\epsilon_2 - \sqrt{3}/2\epsilon_6. \tag{13}$$

These domains are rectangular, 2D lattices with tilted molecules. $\epsilon_2 < 0$ means a compression of the hexagonal lattice along the (NN) direction, while $\epsilon_2 > 0$ corresponds to a stretching along this direction or a compression along the (NNN) orthogonal direction. The tilt direction of molecules is (in a first approximation) linearly related to the strain, $\langle Y_4\rangle = -(\alpha/C_{66}^0)\epsilon_2$, and its direction depends on the sign of the coupling constant α and the bare, shear elastic constant. Since coupling usually decreases the free energy of the system, one may assume $\alpha < 0$, and additionally for the hexagonal LS phase, being a super liquid, one can clearly assume the shear modulus $C_{66}^0 < 0$. Thus, we conclude that the tilt of molecules is expected in the direction of the unit cell compression, a fact that has been experimentally observed, but not explained. This correlation can also be found from considerations involving the elastic dipoles concept and their interaction.[14] We may therefore identify a domain characterized by $\langle Y_4\rangle > 0$ (equivalently $\epsilon_2 < 0$) as one of three domains of the $L_2(L_{2h})$ phase.

IV. THE SWIVELING TRANSITION

The swiveling transition, which has been recently extensively studied,[12,13] is the transition between the $L_2(L_{2h})$ phase [rectangular lattice with molecules tilted towards (NN) direction] and the phase denoted as $L_2'(L_2^*)$ [rectangular lattice, characterized by molecular tilt ordering towards (NNN) direction]. In terms of the order parameters introduced here, the transition corresponds to the change: $\langle Y_4\rangle \Rightarrow -\langle Y_4\rangle$, or equivalent $\epsilon_2 \Rightarrow -\epsilon_2$, for one domain of the phases and with corresponding relations for the two other domains. The domains of the L_{2h} and L_2^* phases can be conveniently represented on the $(\langle Y_4\rangle, \langle Y_5\rangle)$ plane of the orientational order parameters (Fig. 2). They correspond to (local) minima of the free energy function described by Eq. (6). The free energies of the two phases are different and their relative stability is temperature and (strongly) pressure dependent, as shown by experimental studies.[13]

Having identified and characterized the phases which take part in the swiveling transition, it seems the easiest way to analyze the transition would be to consider just one domain of the L_{2h} or L_2^* phase. We may analyze the transition through the cross section of the free energy function for $\langle Y_5\rangle = 0$. This, however, implies that a route for the swiveling transition corresponds to a ''least motion'' path, which may not be true. The transition, most likely, follows a path along lowest energy barriers. In fact, what has been observed recently for fatty acids indicates that the transition goes via an intermediate ''*I*'' phase, where molecules are tilted in an intermediate [between (NN) and (NNN)] direction and the lattice has been identified as oblique.[13] In terms of the order parameters, it indicates that the transition does not go via the $\langle Y_4\rangle \Rightarrow -\langle Y_4\rangle$ route, but rather it corresponds to a path, $\langle Y_4\rangle \Rightarrow 1/2\langle Y_4\rangle + \sqrt{3}/2\langle Y_5\rangle$, e.g., to the nearest domain of another phase. This can be, equivalently, represented as the transition, $[-1/2\langle Y_4\rangle + \sqrt{3}/2\langle Y_5\rangle] \Rightarrow [1/2\langle Y_4\rangle + \sqrt{3}/2\langle Y_5\rangle]$, which has to go via an intermediate state at which $\langle Y_4\rangle = 0$. It implies that the intermediate state with $\langle Y_5\rangle \neq 0$ and oblique lattice $(\epsilon_6 \neq 0)$ can be formed and identified as the *I* phase.

So far, we have not discussed the effect of pressure, but it is known that the swiveling transition is highly surface pressure dependent. One may even view the transition as pressure induced.[13] The question arises as to how isotropic (as usually assumed) the experimentally applied surface pressure π is. If it is isotropic, then the pressure does not couple directly to non-symmetric strain components (or orientational counterparts), but modifies the free energy function by changing the coefficients of the expansion. However, the manner in which this modification appears is not known without numerical calculations for every specific system. An example of such calculations has been presented.[6] If, on the other hand, the surface pressure is not isotropic, it might be considered an anisotropic external stress, $\sigma_2 = \sigma_{xx} - \sigma_{yy}$ or $\sigma_6 = \sigma_{xy}$. The macroscopic stress then couples to macroscopic strain components. For example, considering only one ferroelastic domain characterized by $\epsilon_2 \neq 0$, $\epsilon_6 = 0$, the Gibbs free energy is

$$G(\epsilon_2) = 1/2C_{66}^0\epsilon_2^2 + A'\epsilon_2^3 + B'\epsilon_2^4 + \sigma_2\epsilon_2 \tag{14}$$

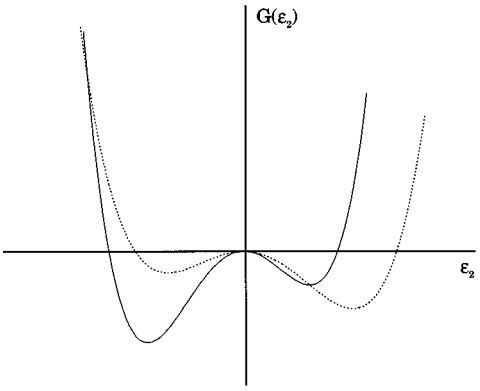

FIG. 3. Schematic representation of the Gibbs free energy, Eq. (14), showing relative stability of the ferroelastic phases.

and the stability of phases will be determined by the sign of the external stress. As indicated in Fig. 3, the phase with $\epsilon_2<0$ is stable under higher external stress.

V. AN INTERNAL STRESS EFFECT

So far, we have considered a system where molecules have been assumed to be cylindrical, e.g., in a rotational state. However, when the molecules experience a strong orientational potential, the rotational dynamics become so slow that the molecular cross sections no longer average to a circle and an orientation of the molecular backbone has to be specified. Therefore, to characterize orientational fluctuations of a molecule in a nonrotational phase, it is helpful to introduce a ''measure'' of the distortion of the cross section from a circular one. One way to do this is by introducing the so-called nematic order parameter, the tensor constructed from a director, as mentioned above. However, it seems more meaningful if the measure of the effective cross section is related to the elastic dipole concept, as introduced into the theory of Langmuir monolayers.[14] With this concept, the orientational fluctuations of a molecule form a distribution of forces around the molecular site. This distribution is conveniently represented by a multipole expansion, where the first term corresponds to a net force, the second to an elastic dipole, and so on. Thus, the elastic dipole has a clear physical meaning and represents an internal (local) stress due to the orientational fluctuations. The internal stress is due to all orientational fluctuations, tilt of molecular tail and backbone orientation and, in principle, should be expressed in terms of Wigner rotation matrices. However, as discussed above, for the Langmuir monolayers it is useful to formally separate the contributions of tilt from the contribution due to backbone orientation. The first contributions have been expressed in terms of surface harmonics as $\langle Y_3\rangle$, $\langle Y_4\rangle$, and $\langle Y_5\rangle$ order parameters. The bilinear coupling between these elastic dipoles and corresponding strains allows for the clear interpretation of the coupling as a stress-strain relation.[14]

The contribution due to the backbone orientation of the molecules is expressed by the same harmonics due to the symmetry constraint. Therefore, a transition from a rotational phase into a nonrotational phase is modeled by introducing an internal stress into the system-the stress created by a frozen orientation of the molecular backbone. The internal stress, being a measure of a difference between the effective cross section and the circular one, can be described by the elastic dipole components $P_2=P_{xx}-P_{yy}$ and $P_6=P_{xy}$ which transform according to the E_2 representation of the C_{6v} group. Thus, the free energy of the system can be described by the equation,

$$F(P,\langle Y\rangle)=F(\langle Y\rangle)+\{P_2\langle Y_4\rangle+P_6\langle Y_5\rangle\}, \tag{15}$$

and the fact that the elastic dipole components P_2 and P_6 are nonzero dictates the broken symmetry of the nonrotational phase. Taking into account the angular form of the orientational order parameters, the free energy function reads,

$$F=B\eta^4-D\eta^6\cos 6\phi+J'\eta^2\cos 2(\phi-\alpha). \tag{16}$$

In the above expression, the elastic dipole components have been expressed as $P_2\propto\cos 2\alpha$ and $P_6\propto\sin 2\alpha$. If, in addition, twofold symmetry is required, $P_6=0$, and the formula becomes

$$F_{\text{twofold}}=J\eta^2\cos 2\phi+B\eta^4\cos 4\phi-D\eta^6\cos 6\phi. \tag{17}$$

This is the same formula used to analyze the swiveling transition.[13] The important point is, as we have shown through the derivation, that the coefficient J has a clear physical meaning—the internal stress representing an orientation of the backbone of the molecule ($J\propto\cos 2\alpha$). Thus, the elastic dipole determines the sign of the coefficient. Analysis of the function as in Eq. (17) shows that the swiveling transition corresponds to a change of the J coefficient ($J>0$, $\alpha=0$; $J<0$, $\alpha=\pi/2$). Moreover, if twofold symmetry is imposed on the system, the possibility to analyze an oblique lattice is ruled out and, in fact, only transitions from rectangular (NN) to rectangular (NNN) lattices can be analyzed. Therefore, not surprisingly, the oblique distortion characteristic for the intermediate I phase could not be analyzed previously.[13]

VI. CALCULATIONS

In order to illustrate the utility of this theory, as well as to confirm its veracity, a series of preliminary calculations were performed. A full potential minimization was performed for a perfectly crystalline monolayer utilizing atom-atom potentials.[6] It should be noted head group interactions and temperature effects have not been modeled. Further, we have departed from the assumptions of previous authors by modeling these phases with only one molecule per unit cell.[12] These calculations were done at a low enough pressure (isotropic) to ensure a global minimum that exhibited tilt (-45 in our arbitrary pressure scale).[6] After locating the potential minimum (with respect to lattice vectors **a** and **b** and the three orientational angles), ϵ_1 was set equal to 0, and a_0 of the parent hexagonal lattice was found by solving the equation

$$\epsilon_1=1/a_0[(2\sqrt{3})a_1\sin\gamma_1+b_1]-2.$$

For any given ϵ_2 and ϵ_6 strains Eq. (2) may subsequently be solved for γ_1, a_1, and b_1. ϵ_2 and ϵ_6 were thus scanned and the three orientational angles were minimized for each point in the (ϵ_2,ϵ_6) plane (Fig. 4). A gradient minimization was

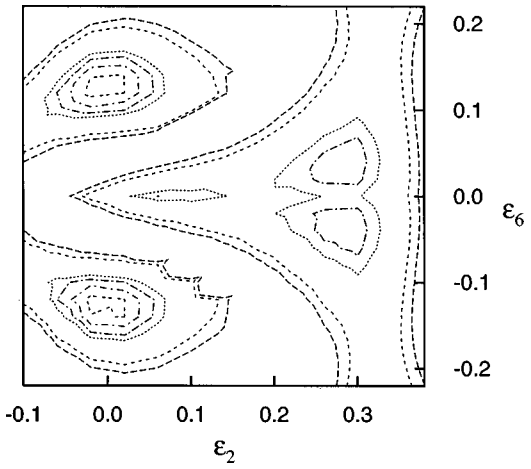

FIG. 4. Potential energy contours of a NNN (L_2^*) phase, showing a threefold minimum.

used, with the starting trial values for any point consisting of the final (minimum) values for an adjacent point. Thus, large deviations from the initial point are not likely to be found, since an energy barrier is likely to be encountered in such a case. In this way, the calculations prefer the ''phase'' of the global minimum. As can be seen from the energy contours in Fig. 4, a threefold minimum is found for this approximately NNN (L_2^*) phase (actual tilt direction $\beta \sim 20°$).

It remained to find a related triply degenerate minimum that resembled a NN (L_{2h}) phase. This was found by setting the lattice to parameters that reflected the minimum near $\epsilon_6 = 0$, $\epsilon_2 = -0.3$, and minimizing all parameters from an initial orientation 90° from that of the previously found minimum. A new minimum was found nearby with $\epsilon_1 = 0.1$, assuming the same a_0 as for the NNN phase. This is reflected in an increase in the area per molecule from 20.16 to 22.11 Å^2. Thus, the relative stability of these two phases should exhibit significant pressure dependence. The results of a scan of the (ϵ_2, ϵ_6) plane are shown in Fig. 5. A similar triple degeneracy is found. In both cases, a slight splitting is observed in the minima located about $\epsilon_6 = 0$. The barrier between these double minima is considerably less than 0.5 kT at room temperature, and will not be observable in practice. This splitting, as well as the departure from the idealized locations of the minima predicted in Sec. II, is directly related to the departure of the molecular geometry from that of a perfect cylinder. Further minima which are also close lying (within 1 kcal/mol) may also be found. While these results demonstrate the concepts related above, and are consistent with both present theoretical and published experimental results, further work is required to establish a more quantitative comparison.

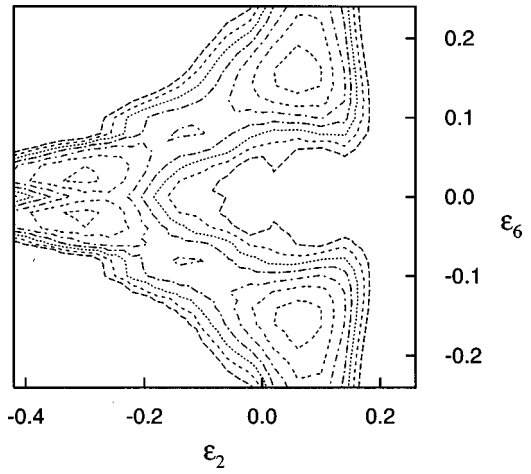

FIG. 5. Potential energy contours of a NN (L_{2h}) phase, showing a threefold minimum distinct from that of the one for a NNN phase.

VII. CONCLUSIONS

We have shown that it is the nature of Langmuir monolayers that the swiveling of molecules must be coupled to a reorientation of the cross sections, as follows from strain-stress (local) coupling. Moreover, we have also shown why the change in the distortion direction tracks the change in tilt direction, thereby answering the question previously posed.[13] In addition, we demonstrated that the phases taking part in the swiveling transition are characterized by the order parameters $\langle Y_4 \rangle$ and $-\langle Y_4 \rangle$, or equivalently ϵ_2 and $-\epsilon_2$ it becomes clear that the cell dimensions in phases L_{2h} and L_2^* are the same, as observed experimentally.[13] It also explains why the axes of the lattices are so insensitive to the cross-section orientation. We have attempted to present a convincing argument that a description in terms of strain-stress couplings, either by macroscopic or local (elastic dipoles), is the easiest way to analyze the complicated phase behavior of Langmuir monolayers as has been demonstrated here for the swiveling transition.

ACKNOWLEDGMENTS

One of the authors (T.L.) acknowledges hospitality of Professor C. J. Eckhardt and his Group, and also support from the Committee for Scientific Research, Poland, for cooperation with the United States. Partial support was also provided by the U.S. Army Research Office through DEPSCOR Grant No. DAAH 04-96-1-0394.

[1] C. M. Knobler and R. C. Desai, Annu. Rev. Phys. Chem. **43**, 207 (1992).
[2] A. M. Bibo, C. M. Knobler, and I. R. Peterson, J. Phys. Chem. **95**, 5591 (1991).
[3] T. Luty and C. J. Eckhardt, J. Phys. Chem. **99**, 8872 (1995).
[4] V. M. Kaganer, I. R. Peterson, R. M. Kenn, M. C. Shih, M. Durbin, and P. Dutta, Chem. Phys. **102**, 9412 (1995), and references therein.
[5] E. B. Sirota, Langmuir **13**, 3849 (1997).
[6] D. Swanson, T. Luty, and C. J. Eckhardt, J. Chem. Phys. **107**, 4744 (1997).
[7] J. V. Selinger and D. R. Nelson, Phys. Rev. Lett. **61**, 416 (1988).
[8] J. V. Selinger and D. R. Nelson, Phys. Rev. A **39**, 3135 (1989).
[9] V. M. Kaganer and E. B. Loginov, Phys. Rev. Lett. **71**, 2599 (1993).
[10] V. M. Kaganer and E. B. Loginov, Phys. Rev. E **51**, 2237 (1995).
[11] E. B. Sirota, H. E. King, D. M. Singer, and H. Shao, J. Chem. Phys. **98**, 5809 (1993).
[12] M. C. Shih, M. K. Durbin, A. Malik, P. Zschack, and P. Dutta, Chem. Phys. **101**, 9132 (1994).
[13] M. K. Durbin, A. Malik, A. G. Richter, R. Ghaskadari, T. Gog, and P. Dutta, Chem. Phys. **106**, 8216 (1997).
[14] T. Luty and C. J. Eckhardt, J. Phys. Chem. **100**, 6793 (1996).